Title
A fundamental study on analyte adsorption onto metallophthalocyanines

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Author
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A FUNDAMENTAL STUDY ON ANALYTE ADSORPTION ONTO METALLOPHTHALOCYANINES

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Chemistry by

Ngoc L. Tran

Committee in charge:
Professor Andrew Kummel, Chair
Professor Robert Cattolica
Professor John Crowell
Professor Douglas Magde
Professor William Trogler

2008
The dissertation of Ngoc L. Tran is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

UNIVERSITY OF CALIFORNIA, SAN DIEGO

2008
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<th>Description</th>
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<tbody>
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<tr>
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This dissertation contains in part or in full, the following publication which has been accepted for publication:


This dissertation contains in part or in full, the following publications which have been submitted or are in final preparation for publication:


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7. N.L. Tran, C.P. Salmon, M.G. Knize and M.E. Colvin; “Experimental and Simulation Studies of Heat Flow and Heterocyclic Amine


**Field of Study**

Major Field: Chemistry (Physical Chemistry)

Studies in Surface Science

Professor Andrew C. Kummel

Major Field: Chemistry (Physical Chemistry)

Studies in Computational Biology

Professor Michael E. Colvin
ABSTRACT OF THE DISSERTATION

A FUNDAMENTAL STUDY ON ANALYTE ADSORPTION ONTO METALLOPHTHALOCYANINES

by

Ngoc L. Tran

Doctor of Philosophy in Chemistry

University of California, San Diego, 2008

Professor Andrew Kummel, Chair

A Web of Science\textsuperscript{1} search shows that the number of articles found in the literature pertaining to Phthalocyanines has doubled in the last eight years alone in comparison to all previous years. Based on the types of articles found, it is clear that the potential applications for Metal Phthalocyanines (MPcs) are multifaceted. Initially, MPcs were used as blue and green dye products.\textsuperscript{2} Subsequent interest in MPcs increased due to its similarities to the biologically relevant porphyrin.\textsuperscript{3,4} More recently, MPcs have been integrated into information storage systems, liquid crystal color displays and as the active material in semiconductor devices.\textsuperscript{5-8} Their diverse electronic properties, chemical and thermal robustness and ease of deposition (spin coating and organic molecular beam epitaxy) make them an attractive and economical candidate for use in chemical sensors.

Although the literature contains many studies pertaining to MPcs, most are focused on the applications aspect of the material or on the fundamental understanding
of the electronic properties of the Pcs in the absence of an analyte. This dissertation attempts to obtain an atomic level understanding of the fundamental mechanisms in which analytes interact with MPcs.

Chapter One uses plane-wave based DFT simulations to compare and contrast the site specific binding of an electron withdrawing analyte, NO, and an electron donating analyte, NH$_3$, to a monomer, trimer and monolayer film Iron Phthalocyanine (FePc). The simulations show that NO chemisorption is restricted to the Fe metal whereas NO physisorption occurs at all nonmetal sites. Additionally, NO physisorption to the pyrrole nitrogens is followed by the barrierless migration of NO to the deep chemisorption well on the Fe metal. In contrast, NH$_3$ only weakly chemisorbs to the Fe metal and does not bind to any other sites. Projected density of states simulations and a Bader analysis of the atomic charges show that the binding of NO to the FePc metal results in a charge transfer from the Fe metal to the NO chemisorbate. The binding of NH$_3$ to the Fe metal results in a smaller transfer of charge in the opposite direction; from the NH$_3$ molecule to the Fe metal. These data are consistent with MPc conductivity and sensor studies.$^{9,10}$ Simulations comparing the binding of NO to the FePc monomer, trimer, and monolayer films showed that both in- and out-of-plane FePc-FePc intermolecular interactions have a negligible effect on the FePc electronic structure and NO binding.

The simulations performed in Chapter One served as a guide for the experimental study in Chapter Two. The King and Wells reflection technique was used to elucidate the chemisorption dynamics of NO on an ordered multilayer FePc film and a quasi-amorphous multilayer tetra-$t$-butyl FePc (ttbu-FePc) film on a
Au(111) substrate. These results were compared to a previous King and Wells study of NO sticking on an ordered monolayer FePc film on a Au(111) substrate.\textsuperscript{11} The NO zero coverage or initial sticking probabilities ($S_0$) were measured as a function of sample temperature ($T_s$) and beam energy ($E_i$). The experimental results for all three films show a monotonic decrease in sticking probability ($S_0$) with increasing sample temperature ($T_s$) and incident beam energy ($E_i$) consistent with NO adsorption via a multiple pathway precursor-mediated mechanism in which the adsorbate initially physisorbs to the FePc organics, diffuses and chemisorbs to the Fe metal center. The NO sticking probability is greatest on the multilayer FePc film and nearly identical between the multilayer ttbu-FePc and monolayer FePc films. This consistent with an increase in collision inelasticity for NO/multilayer FePc/Au(111) compared to NO/monolayer FePc/Au(111). A lower $S_0$ is also observed for the multilayer ttbu-FePc film and is attributed to fewer metal, aromatic, and nitrogen sites being exposed to the incoming beam due to its lower packing density compared to the NO/multilayer FePc film/Au(111). The saturation coverage is also less on the multilayer ttbu-FePc film (2%) than the ordered monolayer and multilayer FePc films (3% for both ordered films), consistent with the area occupied by the Fe metal being less in the lower areal density ttbu-FePc film than in the monolayer and multilayer FePc films.

Chapter Three shifts the focus from the tight binding analytes such as NO to weak binding analytes onto MPcs as weakly bound analytes do not adversely affect device reversibility. DFT simulations with Hartree-Fock exchange was used to more accurately account for these weaker binding systems. The binding strengths of 12 electron donating analytes with a wide range of Lewis basicities were calculated. The
analyte binding strengths were compared to the analytes’ enthalpy of formation with Boron trifluoride (BF$_3$) which is a direct measure of their electron donating ability or Lewis basicity.$^{12}$ With the exception of the most basic analyte investigated, the ZnPc binding energies were found to be a linear function of analyte basicities. Natural population analysis calculations (NPA) showed that analyte complexation to the Zn metal of the ZnPc monomer results in limited charge transfer from the analyte to the ZnPc molecule and increased with analyte-ZnPc binding energy. The ZnPc binding energies were found to be proportional to an exponential of experimentally determined ZnPc sensor sensitivities consistent with sensitivity being proportional to analyte coverage.$^{13}$ The results show that MPcs can make for highly selective sensors since MPcs can even select for analytes with very similar electronic properties. The good correlation observed suggests than DFT is a reliable method to predict MPc binding strengths and relative chemiresistor MPc analyte sensitivities.
CHAPTER ONE

A density functional theory study on the binding of NO onto FePc films

1.1 ABSTRACT

To develop an atomistic understanding of the binding of NO with iron phthalocyanine (FePc), the interaction between NO (an electron withdrawing gas) and NH₃ (an electron donating gas) with an isolated FePc molecule (monomer) was compared with density functional theory (DFT). The simulations show NO strongly chemisorbs to the Fe metal and physisorbs to all the non-metal sites. Additionally, when NO physisorbs to the inner ring nitrogens, NO subsequently undergoes a barrierless migration to the deep chemisorption well on the Fe metal. Conversely, NH₃ only weakly chemisorbs to the Fe metal and does not bind to any other sites. Projected density of states (PDOS) simulations and analysis of the atomic charges show the binding of NO to the FePc metal results in a charge transfer from the Fe metal to the NO chemisorbate; the opposite effect is observed for the binding of NH₃ to the Fe metal. Simulations of NO binding to the Fe metal of a monolayer FePc film
and FePc trimer were also performed to show that intermolecular FePc-FePc interactions have a negligible effect on the FePc electronic structure and NO binding.
1.2 INTRODUCTION

Metallophthalocyanines (MPcs) are square planar molecules that can form highly ordered, chemically inert, and thermally stable films. They have been extensively studied with both experimental—photoemission spectroscopy, reflection high energy electron diffraction, low-energy electron diffraction, scanning tunneling microscopy—and theoretical (Hartree-Fock and density functional theory (DFT)) techniques. Their electronic and absorption properties can be modified by varying the metal center or adding ligands onto the organic rings making them an attractive candidate for use in chemical sensors. Jones and Bott showed that two-terminal resistive sensors with different p-type MPc films (CoPc, CuPc, NiPc, FePc and ZnPc) could be used to discriminate between different electron accepting and electron donating gases at low parts per million concentrations. In addition, Tada et al. showed n-type CuPcF\textsubscript{16}-based organic field-effect transistors were highly sensitive to NH\textsubscript{3}.

Although the experimental and theoretical literature pertaining to MPc sensor applications is extensive, a basic understanding of gas chemisorption onto these metal coordination complexes is lacking. Existing theoretical investigations of MPcs have focused primarily on the electronic structure of the monomer, the film in its β-crystalline form, and the molecular interaction of the monomer with a substrate. A few computational studies have investigated the interaction of an analyte with the MPc but did not allow the MPc-analyte complex to relax geometrically. Of the studies...
that did allow for geometric relaxation, the focus was on analyte binding to the hydrogen bridge of the metal-free phthalocyanine.\textsuperscript{31} When analyte binding to the metal-containing phthalocyanine was studied, site specific binding to the organics was not included.\textsuperscript{32}

In the current study, DFT calculations were used to investigate the site specific interaction of NO and NH\textsubscript{3} with a FePc monomer, trimer, and monolayer film. Analyte binding to the aromatic rings as well as to the metal center of the MPc was investigated. The chemisorption energies for various binding sites on the FePc molecule were evaluated, and all systems were allowed to relax geometrically. The effect of analyte-induced changes on the electronic structure of the FePc monomer were also explored. Simulations comparing the binding of NO to the FePc monomer versus the monolayer film were also performed to investigate the effect of planar interaction on FePc electronic structure and NO binding. To ensure that analyte interaction with the monomer is a reasonable model of analyte interaction with bulk films, NO binding to the FePc trimer was calculated as well.

1.3 COMPUTATIONAL METHOD

Geometry optimizations of all systems (the three FePc systems mentioned above, gas phase NO, gas phase NH\textsubscript{3}, and NO and NH\textsubscript{3} adsorbed onto the three FePc systems) were performed using the Vienna \textit{ab-initio} simulation package,\textsuperscript{33-35} a plane-
wave DFT code with periodic boundary conditions. The DFT simulations were performed with the PW91 variety of the generalized-gradient approximation (GGA), using ultrasoft Vanderbilt pseudopotentials as supplied within VASP\textsuperscript{35-37} and a single k-point (located at the gamma point). To check for saturation of the plane-wave basis, the kinetic energy cutoff was sampled at 50 eV increments from 300 eV to 600 eV for one test case: NH\textsubscript{3} binding to the Fe metal of the isolated, gas-phase FePc molecule. While the binding energy difference between a cutoff energy of 300 eV and 600 eV was more than 0.77 eV, the binding energy difference between a cutoff energy of 400 eV to 600 eV was only 0.052 eV. In consideration of the large number of binding sites and binding configurations investigated in this study and the ~3x computational time required for using the higher energy cutoff, the kinetic energy cutoff was set to 400 eV for simulations of all systems. All systems were geometrically relaxed to a convergence tolerance of 0.01 eV/Å. To account for the open-shell systems, spin polarization was also included in the simulations. The binding energies are calculated as:

\[
E_{\text{binding}} = E_{(\text{FePc + analyte})} - (E_{\text{FePc}} + E_{\text{analyte}})
\]  

(1)

where \(E_{(\text{FePc + analyte})}\) is the total energy of the FePc-analyte complex, \(E_{\text{FePc}}\) is the total energy of the FePc, and \(E_{\text{analyte}}\) is the total energy of the isolated NO or NH\textsubscript{3} analyte.
1.4 RESULTS AND DISCUSSION

A. NO and NH$_3$ binding to the FePc monomer

DFT simulations were used to calculate the binding energies of NO and NH$_3$ onto seven different sites listed as A through G on an isolated FePc molecule (Fig. 1). The isolated FePc molecule will be referred to as the monomer. The monomer was placed in a 20 Å × 20 Å × 15 Å tetragonal unit cell to ensure interactions between FePc molecules in neighboring unit cells are negligible. The optimized FePc monomer has D$_{4h}$ symmetry and simulated bond lengths and angles that agree with previous experimentally and computationally determined values to within 0.02 Å and 1°, respectively.$^{21,38}$ Since the binding energy for NO on the Fe metal of the monomer placed N-end down was 0.94 eV more exothermic than for the O-end down case, binding to all other sites was studied using the N-end down configuration. This is a reasonable assumption considering the N-end of the NO radical contains the more reactive unpaired electron. In addition, numerous studies show an affinity for NO to bind to alkanes and aromatics through the nitrogen.$^{39,40}$

Results of the DFT calculations for NO and NH$_3$ binding onto various sites on the monomer are summarized in Table I. For NO binding onto the Fe metal (site A), the calculations show that NO forms a strong bond to the metal with a well-depth of -1.74 eV. The binding results in an N-Fe bond length of 1.71 Å and a nonplanar FePc molecule (Fig. 2). NO binding to the Fe metal causes the Fe metal to protrude from
the FePc molecular plane toward the NO analyte while the organic rings buckle away from the analyte giving an N-Fe-N bond angle of 162° as compared to 180° for the clean monomer. NO placed on the carbons and nitrogens of the FePc molecule results in weakly bound physisorption ranging from -0.20 eV on the outer ring nitrogen (site G) to -0.23 eV on the organic ring (site D). When NO is placed on the inner ring nitrogen (site B), NO undergoes a barrierless migration from the inner ring nitrogen to the Fe metal in which the binding energy for the final Fe-NO configuration is -1.75 eV. When NO is placed on the inner ring nitrogen (site B) and restricted from migrating to the Fe metal by freezing the NO molecule in the x-coordinate, NO still binds exothermically to the inner ring nitrogen site by -0.25 eV; this is the value for binding site B reported in Table I. In contrast to NO, NH₃ weakly chemisorbs via a nitrogen-end down configuration to the Fe metal (site A) with a modest well-depth of -0.37 eV and does not bind to any other FePc sites.

To better illustrate the role of the Fe metal and aromatics in NO binding, a potential energy surface diagram of NO binding onto the FePc monomer at various binding sites is shown in Fig. 3. The reaction coordinate was calculated based on the distance from the binding site to the metal center. Note that the value reported for the inner ring nitrogen (site B) was calculated with NO frozen in the x-coordinate so as to prevent NO from migrating onto the Fe metal. All other atoms were allowed to relax freely. Despite prohibiting the NO molecule from undergoing any lateral motion, NO binding onto site B still resides on the downward slope of the chemisorption well. These results show that NO can undergo a barrierless migration from site B to the Fe
metal. In addition, barriers to migration from organic site to organic site (F to E, E to D and D to C) and to the inner ring nitrogen site (C to B) were calculated by freezing the NO molecule at each halfway point between binding sites and allowing the FePc monomer to relax. As seen in Fig. 3, the barriers to migration from organic site to organic site and from organic site to the inner ring nitrogen site are on the order of 0.23 eV (F to E) to 0.11 eV (C to B) and, at temperatures above 77 K, can be easily overcome. In sum, NO can migrate with small barriers from the organic ring sites suggesting the FePc molecule acts to funnel NO to the deep chemisorption well on the Fe metal.

The simulated well-depths suggest NO binds weakly to the FePc organics and tightly to the FePc metal. This is consistent with a thermal desorption study where two peaks were observed for the non-dissociative, molecular desorption of NO from a β-polymorph FePc powder.\textsuperscript{41} The authors suggest that the high temperature peak corresponds to NO desorption from the Fe metal center. Based on Redhead’s peak maximum method for first order desorption, the higher temperature desorption peak corresponds to an adsorption energy of 1.2 eV.\textsuperscript{42} Note that hopping between sites is not taken into account in this model. In the case of NO on FePc, a multiple stage desorption path may exist whereby NO initially diffuses from the Fe metal and into the physisorption well on the organics. The DFT calculated barrier to diffusion from the Fe-metal to the organics is about 1.5 eV suggesting the chemisorption energies predicted in this study are overestimated by 0.3 eV. The overestimation may be a result of the artificial, gross structural relaxation incurred by the isolated, single
molecule FePc upon NO adsorption. However, this can be excluded because simulations of NO adsorption on a triple stack FePc, where gross structural relaxations are absent, predict binding energies that are very similar to the isolated monomer (see section C below). Most likely, the discrepancies observed in the DFT predicted and thermal desorption calculated adsorption energies are an artifact of the functional used in this study. Becke performed a comprehensive test of 55 systems and showed that for these tightly bound systems GGA overbinds by 0.2 eV on average.43 Despite the errors in these simulations, a qualitative conclusion can still be derived from these results where NO has a strong affinity to bind to the Fe metal as opposed to the organic ring but the organic rings acts as precursor sites for chemisorption to the metal centers.

These simulated binding energies are also consistent with recent King and Wells sticking probability measurements for NO on a monolayer FePc on a Au(111) substrate.11 The sticking experiments show NO saturation occurs at 3% of a monolayer for various beam energies and surface temperatures. Since the metal represents about 3% of a monolayer, this is consistent with the DFT simulations described in this paper showing chemisorption occurring only at the Fe metal. Additionally, the data show the initial sticking probability ($S_0$) is large (40%) at low translational beam energy and low surface temperature. As the NO translational energy and surface temperature are increased, the initial sticking probability decreases linearly until at 300 K $S_0$ is 0% for the highest beam energy. The monotonic decrease in sticking probability as surface temperature and incident beam energies are increased
is consistent with NO trapping onto physisorption sites on the monolayer. These data are also consistent with the calculated well-depths for NO binding onto the aromatics of the FePc monomer (~0.2 eV exothermic). Both the simulations and sticking data strongly suggest NO adsorbs onto a monolayer FePc via multiple precursor-mediated physisorption pathways where it initially adsorbs onto the aromatics and subsequently diffuses and chemisorbs only onto the metal centers.

B. NO and NH₃ induced changes in the FePc monomer electronic structure

Many sensor studies have suggested electron withdrawing gases (such as NO) inject holes into these $p$-type MPc films, thus increasing film current.⁴⁴ A study by Nyokong and Vilakazi showed that FePc modified electrodes gave the largest current increase upon NO oxidation when compared to the metal-free H₂Pc and various other metallated MPcs suggesting the NO and FePc interaction is strong.⁴⁵ The opposite effect is observed by electron donating gases (such as NH₃) where a decrease in film current is observed and attributed to trapped charge carriers.⁴⁶ An analysis of the total density of states (DOS) and projected density of states (PDOS) of the FePc monomer before and after NO and NH₃ adsorption onto the Fe metal shows that both analytes can induce a change in the FePc electronic structure. Since the states closest to the Fermi level ($E_F$) will most affect conductivity in the film, only the states in the energy range from -2.0 eV to 2.0 eV will be analyzed. The DOS of the FePc monomer prior to analyte adsorption [Fig. 4(a)] contains a partially filled state at the Fermi level ($E_F$)
and an unfilled state centered at 0.53 eV. The Fe PDOS shows that these states are localized on the Fe atom. The presence of a partially-filled state at $E_F$ is also consistent with orbital-mediated tunneling spectroscopy measurements of CoPc and Cobalt tetraphenylporphyrin, a Pc analog, on a Au(111) substrate whereby a mid-gap state exists for both organometallic films.$^{47}$ The Fe localized nature of this state suggests FePc monolayer films are semiconducting, consistent with numerous sensing studies.$^{48}$

NO binding to the Fe metal of the monomer [Fig. 4(b)] induces an obvious change in the monomer electronic structure. Upon NO chemisorption onto the Fe metal of the FePc monomer, the mid-gap Fe state is shifted into the filled state centered at -0.57 eV. The lowest energy unfilled Fe state shifts from 0.53 eV to the higher energy state at 0.93 eV. Upon NH$_3$ adsorption onto the Fe metal, Fig. 4(c) shows the mid-gap Fe state at $E_F$ is shifted into the filled state centered at -0.33 eV. The lowest energy unfilled Fe state shifts from 0.53 eV to the lower energy state at 0.43 eV. While the DFT calculations clearly show that NO and NH$_3$ adsorption to the Fe metal induces a change in FePc electronic structure, it is difficult to relate how these changes correspond to changes in MPc sensor response.

The PDOS of the clean FePc monomer for the nonequivalent carbon and nitrogen atoms also resembles that observed by Bialek but is not discussed here since adsorption of either analyte at all carbon and nitrogen sites does not induce significant changes in these PDOSes.$^{49}$
The analyte induced changes in MPc conductivity can be predicted from the calculated DOS by showing that charge transfer complexes are formed when electron withdrawing or electron donating gases interact with the MPc film. An analysis of the atomic charges of the FePc monomer before and after NO and NH₃ adsorption using the Bader charge distribution method shows that charge transfer occurs between the adsorbate and FePc monomer. Upon NO adsorption, the Fe metal loses 0.28e⁻ while the NO molecule gains 0.31e⁻, consistent with the electron withdrawing nature of NO. In contrast, the weak binding of NH₃ to the Fe metal results in a gain of 0.06e⁻ for the Fe metal and a loss of 0.07e⁻ for the NH₃ molecule, also consistent with the electron donating nature of NH₃. For both analytes, only a slight transfer of charge was observed for binding onto the non-metal sites (less than ±0.03e⁻). This is expected since the simulations show NO only weakly binds to the non-metal sites and NH₃ only binds to the metal. The calculated charge transfer is consistent with experimental results showing NO increases while NH₃ decreases the current in p-type MPc films.

C. NO binding to the Fe metal of the FePc trimer

To investigate the effect of out-of-plane FePc-FePc intermolecular interactions on the FePc electronic structure and analyte binding, simulations of NO sticking to the Fe metal of an FePc triple stack was performed. NO binding only to the Fe metal site of this system was investigated since NO binding to the Fe metal of the FePc
monomer gave the greatest analyte-FePc interaction. In addition, binding to the metal center should be most perturbed by FePc-FePc out-of-plane interactions.

The adsorption energy of NO onto the Fe metal of a triple stack FePc was calculated. The triple stack FePc system will be referred to as the FePc trimer, and a schematic of this system can be found in Fig. 5(a). The FePc trimer was placed in a 20 Å × 20 Å × 15 Å tetragonal unit cell to ensure interactions between FePc molecules in neighboring unit cells are negligible. FePc-FePc z-spacing in the trimer was set to 3.4 Å and the N-Fe-N bond angle for all three FePc layers was 180° prior to relaxation, in accordance with experimentally determined values. The bottom FePc layer of the trimer was geometrically frozen to imitate FePc in the bulk. The relaxed trimer had average simulated Fe-Fe and phenyl-phenyl z-spacings of 3.44 Å and 3.50 Å, respectively [Fig. 5(a)]. These values resemble the experimentally determined value of 3.4 Å suggesting the FePc trimer is a good model of a thick FePc film.

A double stack FePc system (dimer) was also calculated where both the top and bottom FePc layers were allowed to relax. The dimer resulted in simulated Fe-Fe and phenyl-phenyl z-spacings and bond angles that differ from the experimentally determined values by more than 30% suggesting the FePc dimer may not be the most appropriate system to model a thick FePc film. Since the FePc dimer is a poor model of a multilayer FePc film, NO binding to the Fe metal of the dimer will not be discussed.
The simulations show NO adsorption to the Fe metal of the trimer is similar to NO adsorption to the Fe metal of the monomer. NO adsorption to the Fe metal of the trimer results in a well-depth of -1.67 eV, which is nearly equivalent to NO adsorption to the monomer metal center. Analogous to the monomer calculation, the trimer calculations show NO binding to the top-most Fe causes the Fe metal to protrude out of the FePc molecular plane [Fig. 5(b)] resulting in an Fe-N(O) bond distance of 1.74 Å and N-Fe-N bond angle of 167°. However, unlike NO binding to the monomer, the organic rings in the top layer of the trimer do not buckle away from the analyte. Most likely, interactions with the organics in the middle and bottom layers of the trimer prohibit the top organic layer from bending away from the analyte. This results in an average phenyl-phenyl z-spacing of 3.54 Å. In addition, the average Fe-Fe z-spacing has increased marginally to 3.59 Å.

Similar to the FePc monomer, chemisorption of NO onto the Fe metal of the FePc trimer induces a change in its electronic structure. Figure 6(a) shows the Fe PDOS of each layer of FePc labeled as top, middle and bottom before NO adsorption onto the Fe metal of the top FePc layer. The Fe PDOSes of the individual layers in the trimer closely resembles that observed in the monomer where all three layers contain a partially-filled Fe state at mid-gap and an unfilled Fe state in the conduction band at 0.48 eV. Similarity in the Fe PDOSes of the monomer and trimer suggests Fe-Fe interactions in thick FePc films are small. As seen in Fig. 6(b), binding of NO to the Fe metal of the top FePc layer results in an electronic structure change similar to that observed in the FePc monomer but this change is confined to the Fe metal of the top
FePc layer. The mid-gap Fe state is shifted into the filled state centered at -0.31 eV. The lowest energy unfilled state is shifted from 0.42 eV to the higher energy state at 0.73 eV. The PDOS of the Fe metal for the FePc middle and bottom layers remain relatively unchanged after NO adsorption suggesting FePc-FePc interactions are weak and do not significantly affect binding to the metal center. Again, the highly localized nature of the Fe PDOSes in the trimer strongly suggests MPc films are semiconducting, consistent with numerous experimental studies.

Analysis of the atomic charges of the FePc trimer before and after NO adsorption onto the Fe metal using the Bader charge distribution method shows there is a transfer of charge between the adsorbate and FePc trimer. When NO adsorbs onto the Fe metal, the Fe metal directly interacting with NO loses 0.26e\textsuperscript{-} while the NO molecule gains 0.27e\textsuperscript{-}. This oxidation of the Fe metal is consistent with experimental results showing NO increases the current in p-type MPc films. Additionally, these values are comparable to that observed for the FePc monomer and further suggests out-of-plane FePc-FePc intermolecular interactions do not affect NO binding.

D. NO binding to the Fe metal of the FePc monolayer film

To investigate the effect of FePc-FePc in-plane interactions, the adsorption energy of NO onto the Fe metal of an FePc monolayer film was calculated. A schematic of the monolayer film is shown in Fig. 7(a). The monolayer film was placed in a 13.7 Å x 13.7 Å x 15 Å tetragonal unit cell and was modeled based on a
monolayer FePc on a 23 x \( \sqrt{3} \) Au(111) surface.\(^{18}\) The Au substrate was not included in these simulations since even FePc-FePc bonding leaves the NO chemisorption energy unchanged as discussed above. The optimized FePc monolayer film also has \( D_{4h} \) symmetry and simulated bond lengths and bond angles that agree with the values obtained for the simulated monomer to within 1%. The simulated chemisorption well-depth for NO adsorption to the Fe metal of the FePc monolayer is nearly identical to that obtained for the monomer and trimer (-1.69 eV). NO binding results in an Fe-N(O) bond length of 1.73 Å and, like that observed in the monomer and trimer, the FePc molecule relaxes around the NO to give an N-Fe-N bond angle of 161°.

Chemisorption of NO onto the Fe metal of the FePc monolayer induces a change in its electronic structure similar to that observed in the FePc monomer and trimer. Figure 8 shows the Fe PDOS of the FePc monolayer before and after NO adsorption onto the Fe metal. The Fe PDOS of the monolayer contains a partially-filled state at mid-gap and an unfilled state centered at 0.59 eV. When NO binds to the Fe metal of the FePc monolayer, the mid-gap Fe state is shifted into the filled state centered at -0.40 eV. The lowest energy unfilled Fe state is shifted from 0.59 eV to the higher energy state centered at 1.28 eV. The similarity in electronic structure changes upon NO adsorption to the metal of the FePc monolayer and monomer suggests in-plane FePc-FePc interactions do not affect analyte binding to the metal center.

Analysis of the atomic charges of the FePc monolayer before and after NO adsorption onto the Fe metal using the Bader charge distribution method shows there
is a transfer of charge between the adsorbate and FePc monolayer. When NO adsorbs onto the Fe metal, the Fe metal loses 0.25e⁻ while the NO molecule gains 0.26e⁻ consistent with experimental results showing an increase in current in p-type MPc films upon exposure to NO. These values are comparable to that observed in both the FePc monomer and trimer suggesting in-and out-of-plane FePc-FePc interactions have a negligible effect on NO binding.

1.6 CONCLUSIONS

Electron withdrawing (NO) and electron donating (NH₃) analyte binding to the metal center and aromatic rings of the FePc were investigated. The simulations show NO strongly chemisorbs to the Fe metal center and physisorbs to all other non-metal sites. Conversely, NH₃ only weakly chemisorbs to the Fe metal center. NO can undergo a barrierless migration from some of the physisorption sites to the deep chemisorption well on the iron metal center consistent with molecular beam sticking measurements. PDOS simulations show the binding of NO and NH₃ to the FePc metal center results in a transfer of charge between the Fe metal and analyte consistent with multiple conductivity and sensor experiments. Simulations comparing the binding of NO to the FePc monomer, trimer and monolayer film showed that both in- and out-of-plane FePc-FePc intermolecular interactions have a negligible effect on FePc
electronic structure and NO binding suggesting the FePc monomer is a sufficient model of the FePc film.
Figure 1.1 Schematic of FePc monomer showing the seven binding sites investigated (A-G).
Figure 1.2  Schematic of NO binding onto the metal center of the FePc monomer. The N-Fe-N bond angle changes from 180° to 162° upon NO chemisorption. The resulting Fe-N(O) bond length is 1.71Å.
Figure 1.3  Potential energy surface diagram of NO binding at various sites on the FePc monomer. Solid circles = binding energies for NO to Fe metal (A) and non-metal physisorption sites (B-F). Open squares = barriers to diffusion from site to site. The line connecting the points acts only as a guide.
Figure 1.4 Solid line represents FePc DOS and solid squares represent Fe projected DOS of the (a) clean FePc monomer, (b) NO adsorbed to the Fe metal of the FePc monomer and (c) NH₃ adsorbed to the Fe metal of the FePc monomer.
Figure 1.5  Schematic of (a) the relaxed FePc trimer and (b) NO binding to the Fe metal of the FePc trimer. NO binding to the Fe metal gives an N-Fe-N bond angle and Fe-N(O) bond length of 167° and 1.74 Å, respectively.
Figure 1.6 Solid squares, open circles and shaded line represents Fe PDOS of the TOP, MIDDLE and BOTTOM FePc, respectively, for the (a) clean FePc trimer, and (b) NO adsorbed to the Fe metal of the trimer.
Figure 1.7  Top down schematic of FePc monolayer.  \( a = b = 13.7 \text{Å} \)
Figure 1.8  Solid line represents Fe PDOS of the clean monolayer and solid squares represent Fe PDOS for NO adsorbed onto the Fe metal of the FePc monolayer. Since the DOS of the monolayer is similar to that observed for the monomer and trimer, the monolayer DOS is not shown.
Table 1.1 Table of simulated binding energies for NO and NH3 on the FePc monomer at all seven sites. The value reported for NO binding to Site B is for the NO molecule prohibited from migrating to the Fe metal center.

<table>
<thead>
<tr>
<th>Analyte binding sites</th>
<th>NO (eV)</th>
<th>NH3 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Fe center</td>
<td>-1.74</td>
<td>-0.37</td>
</tr>
<tr>
<td>(B) Inner ring nitrogen</td>
<td>-0.25</td>
<td>-0.01</td>
</tr>
<tr>
<td>(C) Organic</td>
<td>-0.20</td>
<td>-0.03</td>
</tr>
<tr>
<td>(D) Organic</td>
<td>-0.23</td>
<td>-0.02</td>
</tr>
<tr>
<td>(E) Organic</td>
<td>-0.23</td>
<td>-0.02</td>
</tr>
<tr>
<td>(F) Organic</td>
<td>-0.21</td>
<td>-0.02</td>
</tr>
<tr>
<td>(G) Outer ring nitrogen</td>
<td>-0.20</td>
<td>-0.03</td>
</tr>
</tbody>
</table>
1.9 Acknowledgments

This chapter has been published:

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CHAPTER TWO

NO CHEMISORPTION DYNAMICS ON THICK FEPC TTBU- FEPC FILMS

2.1 ABSTRACT

The NO chemisorption dynamics on ordered multilayer iron phthalocyanine (FePc) and quasi-amorphous multilayer tetra-t-butyl FePc (ttbu-FePc) films on a Au(111) substrate were investigated using the King and Wells reflection technique. The NO zero coverage or initial sticking probabilities ($S_0$) were measured as a function of sample temperature ($T_s$) and beam energy ($E_i$). The experimental results for both films show a monotonic decrease in $S_0$ with increasing $T_s$ and $E_i$ consistent with NO adsorption via a multiple pathway precursor-mediated mechanism in which the adsorbate initially physisorbs to the FePc organics, diffuses and chemisorbs to the Fe metal center. The saturation coverage is 3% for the multilayer FePc surface and only 2% for the multilayer ttbu-FePc surface. The reduced saturation coverage in the ttbu-FePc film is attributed to fewer Fe metal centers in the less dense ttbu-FePc films. A comparison of NO sticking on a multilayer FePc/Au(111) film with NO sticking on a monolayer FePc/Au(111) film shows that $S_0$ is greater on the multilayer FePc film for all $T_s$ and $E_i$, consistent with an increase in collision inelasticity for NO/multilayer FePc/Au(111).
2.2 INTRODUCTION

Metallophthalocyanines (MPcs) are a group of square planar, metal coordination complexes in which a metal atom is bound by four pyrrole nitrogens linked to aromatic rings. MPcs can form highly ordered films, and are chemically and thermally resilient. Initially, most studies on MPcs either focused on their use as blue and green dyestuffs or compared their properties to similar organometallics, such as porphyrins. MPcs are an attractive candidate for use in chemical sensors because a simple change of the metal atom or substitution to the aromatics changes the gas chemisorption properties. There are numerous studies on gas-induced changes in the MPC electronic structure but few studies on gas chemisorption dynamics on MPcs. While a few sensor studies have focused on the different interactions of weak and strong binding analytes to MPcs, nearly all experimental studies on MPC sensors neglect the basic mechanisms by which analytes absorb onto and react with MPcs.

Recently, the King and Wells reflection technique has been used to investigate NO chemisorption dynamics on a monolayer FePc film in ultra high vacuum (UHV). The experimental results are consistent with NO adsorbing to the monolayer FePc via a multiple pathway precursor-mediated mechanism in which the adsorbate first physisorbs to the FePc organics, then diffuses and chemisorbs to the Fe metal center. These findings were supported by density functional theory (DFT) simulations.
showing NO chemisorbs to the Fe metal center and physisorbs to all other non-metal sites. The DFT calculations showed the barrier to NO diffusion between MPc adsorption sites on each MPc molecule was small suggesting that, at 300K, NO can diffuse from the physisorption sites to the deep chemisorption well on the Fe metal.

The aforementioned study on NO/MPc chemisorption dynamics reported the sticking probability of NO on ordered monolayer FePc films, but MPc-based gas sensors are fabricated with multilayer MPc films. This manuscript reports the effect of varying the nature of FePc-FePc interactions by measuring the NO sticking probabilities ($S_0$) on ordered multilayer FePc and quasi-amorphous multilayer ttbu-FePc films as a function of sample temperature ($T_s$) and incident beam energy ($E_i$). In addition, the effect of FePc-FePc interactions versus FePc-Au(111) substrate interactions on adsorbate reactivity is investigated by comparing $S_0$ on the multilayer films versus $S_0$ on the ordered monolayer FePc film.

### 2.3 EXPERIMENTAL METHODS AND TECHNIQUES

The UHV chamber and molecular beam apparatus used in this study has been described in detail elsewhere. A single crystal Au(111) substrate (Monocrystals, Inc.) was cleaned and ordered by sputtering with 2 kV Ar$^+$ ions followed by annealing the surface to 775 K for five minutes. Auger electron spectroscopy (AES) verified the Au surface was free of impurities and low energy electron diffraction (LEED) showed
the surface order consisted of the expected $\sqrt{3} \times 22$ hexagonally closed-pack reconstruction.\textsuperscript{70,71}

**A. Multilayer FePc**

The Fe(II)Pc was purchased from Sigma-Aldrich and purified by repeated degassing in the UHV chamber until the chamber pressure was below $10^{-7}$ Torr during deposition. A schematic of an FePc molecule can be found in Fig. 1(a). A multilayer FePc film was deposited onto the room temperature Au(111) substrate by maintaining a cell temperature of 615 K for five minutes (Createc low-temperature effusion cell LTC-40-20-SH-M). The film was flash annealed to 375 K to desorb any residual contaminants remaining on the surface. Flash annealing the sample also facilitates in the formation of an ordered thick film that lies parallel to the substrate surface as demonstrated by various STM and LEED studies.\textsuperscript{72,73} The presence of a surface plane lying parallel to the substrate is important in this study since this exposed configuration allows the central Fe metal atom, the pyrrole- and meso- nitrogens, and aromatics of the FePc molecule to freely interact with the incoming NO molecules. The AES spectrum of this surface consists of the expected carbon to nitrogen ratio of 4:1.\textsuperscript{56} The Au peak is absent and consistent with the presence of a thick FePc film. The LEED pattern of the multilayer film taken at 15 eV results in the signature MPc/Au(111) diffraction pattern containing a superposition of three rotationally equivalent domains.\textsuperscript{74} The Au diffraction pattern was not observed also confirming the presence of a thick film.
B. Quasi-Amorphous Multilayer ttbu-FePc

2(3),9(10),16(17),23(24)-Tetrakis-(tert-butyl)-phthalocyaninato iron (II), which will be referred to as tetra-\textit{t}-butyl FePc (ttbu-FePc) in this study, was synthesized according to literature procedures.\textsuperscript{75,76} For ttbu-FePc, each of the outer carbon rings has one \textit{t}-butyl ligand randomly substituted for one of the hydrogens; therefore, the ttbu-FePc forms an amorphous bulk structure. A schematic of the substituted ttbu-FePc can be found in Fig. 1(b). 2.01 g of 1,2-Dicyano-4-\textit{tert-}
butylbenzene (10.9 mmol) was dissolved in dry \textit{N},\textit{N}-dimethylaminoethanol (DMAE) with 1.53 g of iron (II) sulfate heptahydrate (5.43 mmol) and 0.5 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The solution was refluxed for 16 hrs. The product was cooled and precipitated in a 50:50 water/methanol solution, suction filtered, and washed several times with the 50:50 water/methanol solution. The resulting blue-black solid was further purified by Soxhlet filtration in acetone. The yield was 35%. The ttbu-FePc was initially purified by rough pumping at a sample temperature of 325 K. This was followed by a second purification process in which the sample was repeatedly degassed in the UHV chamber until the chamber pressure was below 10\textsuperscript{-7} Torr during deposition. The multilayer ttbu-FePc film was deposited onto the room temperature Au(111) substrate for two minutes at a cell temperature of 625 K and annealed at 575 K to desorb any residual contaminants from the film. Note that this annealing temperature is below the temperature at which ttbu-FePc sublimes. The AES spectrum of this surface results in the expected carbon to
nitrogen ratio of 6:1 and an absence of the Au peak suggesting the presence of a thick film. No LEED pattern was observed for this surface indicating the ttbu-FePc film is at least partially amorphous. LEED is only sensitive to ordered domains in the x-y plane of about 90 nm so there may still be short-range order within the ttbu-FePc film. The higher energy residual pattern of the Au substrate was also not observed consistent with the presence of a thick film.

The lack of order in the ttbu-FePc film agrees with Biswas et al where they also found tetra-t-butyl substituted MgPc formed a disordered thin film on Au(100) using PES. In contrast to LEED and PES, filled-state STM imaging of a multilayer ttbu-NiPc film on Au(111), as shown in Fig. 2(a), clearly shows substituted multilayer MPc films are not completely amorphous. The image was taken with a -1.0 V sample bias and 0.5 nA tunneling current. The quasi-amorphous film was prepared by depositing ttbu-NiPc at 725 K for 3 minutes onto a room temperature Au(111) substrate followed by post-deposition annealing at 544 K for 15 minutes. Although the ttbu-NiPc surface layer is missing the orientational and periodic long-range order that is observable by LEED, the STM image shows that it still has a nearly planar structure such that most of the Fe metal centers, nitrogens and aromatics are available for gas adsorption as in the ordered, multilayer FePc film.

A rough estimate of the areal density of flat-lying ttbu-NiPc molecules can be extrapolated from the STM image by measuring the distance between the irregular rows of ttbu-NiPc molecules. Numerous line scans on an 800 Å × 800 Å ttbu-NiPc/Au(111) film were measured to give an average ttbu-NiPc row to row distance of
20.2 ± 3.7 Å. Using 20.2 ± 3.7 Å as the square planar lattice constant for the ttbu-NiPc film, the maximum area occupied by a single ttbu-FePc molecule is estimated as 408 Å². Alternatively, a minimum areal density for ttbu-FePc is estimated by assuming an asymmetric unit cell made up of the ttbu-MPc/Au(111) row spacing and MPc/Au(111) lattice constant since the spacing within the ttbu-MPc row may be smaller than the spacing between the rows. The filled-state, monolayer CuPc/Au(111) STM image in Fig. 2(b) (-1.0 V sample bias and 0.5 nA tunneling current) has a square lattice of 15.4 Å x 15.4 Å, in good agreement with Chizhov et al. Using this lattice constant value with the ttbu-MPc/Au(111) row spacing, the estimated minimum areal density for a ttbu-FePc molecule is 311 Å². Therefore, surface ttbu-FePc molecules have an areal density between 24% to 42% lower than FePc molecules in the ordered monolayer or multilayer FePc films on Au(111).

C. King and Wells measurements

The sample temperature was controlled by liquid nitrogen cooling and radiative heating from the back side of the sample with a thoriated iridium ribbon filament. Tₛ was varied from 100 – 300 K in 25 K increments. Supersonic NO molecular beams were directed at a normal angle to the FePc surface. NO was mixed with helium and neon to vary Eᵢ; three translational beam energies were investigated: 0.4, 0.26 and 0.09 eV.¹¹

The King and Wells beam reflectivity technique was employed to measure S₀. Two beam blocks are used: a gate valve to completely block the molecular
beam from entering the UHV chamber, and when the gate valve is open, an inert
Pyrex flag to block the beam from impinging on the FePc surface. $S_0$ is calculated as
the ratio of the partial pressure drop, $\Delta P(t_1)$, when the flag is removed at $t_1$, allowing
the beam to strike the sample surface divided by the partial pressure rise, $\Delta P(t_0)$, when
the gate valve is initially opened at $t_0$, allowing the beam to enter the UHV chamber:

$$S_0 = \frac{\Delta P(t_1)}{\Delta P(t_0)}$$

Equation 1

Since NO adsorbs to phthalocyanine, an immediate partial pressure drop is
observed as seen in Figure 3. In the case of NO adsorption onto MPcs films,
saturation occurs rapidly (on the order of 1 – 2 seconds) resulting in the sharp,
downward spike. A detailed discussion of NO saturation on MPc films is presented
below in the Results and Discussion section B.

2.4 RESULTS AND DISCUSSION

A. NO sticking on ordered multilayer FePc, multilayer ttbu-FePc and
monolayer FePc films

$S_0$ on the ordered multilayer FePc film versus $T_s$ for all three NO beam
energies are shown in Fig. 4(a). Note that NO sticking onto the Au(111) surface does
not contribute to the $S_0$ values because NO does not stick to Au at these
temperatures.\textsuperscript{11,80} NO sticks to the multilayer film with $S_0 = 0.43 \pm 0.01$ at the lowest $E_i = 0.09$ eV and $T_s = 100$ K. Increasing $E_i$ decreases $S_0$ to $0.38 \pm 0.01$ and $0.35 \pm 0.01$ for the 0.26 eV and 0.40 eV beams at 100 K, respectively. Increasing $T_s$ linearly decreases the sticking probability such that $S_0 = 0.14 \pm 0.01$ at 300 K for the 0.09 eV beam. A similar linear decrease in $S_0$ as a function of increasing $T_s$ is also observed at higher beam energies. NO sticking even at 300 K is consistent with a final chemisorbed state since physisorbates are not stable on the surface at 300 K. A direct chemisorption model to explain NO adsorption onto the ordered multilayer FePc film can be excluded since direct chemisorption requires $S_0$ to be independent of $T_s$ and $E_i$. Instead, the strong dependence of $S_0$ on $E_i$ and $T_s$ observed in this study is consistent with NO precursor-mediated chemisorption onto the ordered multilayer FePc film. In the standard model of precursor-mediated chemisorption, NO traps onto the film prior to chemisorption; an increase in $E_i$ or $T_s$ decreases the trapping probability and an increase in $T_s$ also increases the desorption probability of NO from the trapped state prior to chemisorption.\textsuperscript{81-83}

To examine the effect of varying the nature of FePc-FePc interactions with FePc on Au(111) substrate interactions, $S_0$ of the 0.4 eV NO beam versus $T_s$ onto an ordered multilayer FePc, quasi-amorphous multilayer ttbu-FePc, and ordered monolayer FePc film versus $T_s$ is shown in Fig. 4(b).\textsuperscript{1} $S_0$ is greater on the ordered multilayer FePc film ($0.35 \pm 0.01$) than on both the multilayer ttbu-FePc ($0.24 \pm 0.03$)
and monolayer FePc films (0.24 ± 0.01) at 100 K. This trend is also observed at higher T, where S0 for the ordered multilayer and quasi-amorphous multilayer films are 0.099 ± 0.006 and 0.011 ± 0.008 at 300 K, respectively. S0 is greater on the ordered multilayer FePc film than on the ttbu-FePc and monolayer FePc films at all T, and Ei whereas S0 for the monolayer FePc and ttbu-FePc films are nearly identical at all T, and Ei. While the overall sticking of NO to the multilayer ttbu-FePc film and monolayer FePc films are less than to the ordered multilayer FePc film, NO adsorption onto the ttbu-FePc and monolayer FePc films show a similar trend whereby increasing T, linearly decreases S0. The monotonic decrease in S0 with increased T, suggests NO undergoes precursor-mediated chemisorption onto all three films.

For NO sticking onto the multilayer ttbu-FePc film, the lower S0 at all T, and Ei may be due to a more convoluted path to diffusion between the physisorption and chemisorption sites and due to a lower density of each type of adsorption site. The addition of t-butyl ligands on the aromatics may create additional NO physisorption sites in a system that already possesses six distinct physisorption sites in the form of the aromatics and the meso- and pyrrole-nitrogens.64 However, the bonding of NO to the relatively non-reactive t-butyl carbons is likely to be weaker than to the aromatic sites. Moreover, the nearly identical temperature dependence of S0 for both the ordered thick FePc and quasi-amorphous ttbu-FePc films is most consistent with the t-butyl ligand being inert to NO physisorption over the full temperature range studied. Therefore, the lower S0 on the thick ttbu-FePc film is primarily attributed to fewer
metal, aromatic, and nitrogen sites being exposed to the incoming beam due to its lower packing density.

For NO sticking onto the ordered monolayer FePc films, the lower \( S_0 \) is consistent with a greater NO trapping probability on the ordered multilayer FePc film due to enhanced inelastic collisions in the effectively lighter multilayer FePc/Au(111) film compared to the heavier monolayer FePc/Au(111) film. As shown in Fig. 5(a, b), plotting the NO sticking probability as a function of NO beam energy for both the ordered monolayer and ordered multilayer FePc films shows a linear dependence of \( S_0 \) on \( E_i \). Linearly fitting the \( S_0 \) as a function of \( E_i \) at 100 K for the multilayer FePc film/Au(111) gives a slope of -0.28. Increasing \( T_s \) to 200 K and 300 K decreases the slope to -0.20 and -0.13. As shown in Fig. 5(b), the same fit for NO sticking onto the monolayer FePc film/Au(111) at 100 K results in a slope of -0.47 or 1.7 times greater than for the ordered multilayer FePc film. Increasing \( T_s \) to 200 K also results in a slope that is 1.7 times greater than for the ordered thick film until, at 300 K, the slopes are nearly identical. The equivalent slopes at 300 K suggests that at higher \( T_s \), the NO trapping probability onto the ordered multilayer FePc and monolayer FePc films is no longer a crucial factor in NO adsorption onto these films. However, the differences in slopes at lower \( T_s \) are consistent with a higher density of soft phonon modes in the multilayer FePc film compared to the monolayer FePc film. By examining the effective mass difference between the ordered films, a qualitative comparison of the collision elasticity can be made. The effective mass of the Fe metal chemisorption site on the multilayer FePc/Au(111) can be calculated by adding the mass of the Fe metal.
center of the surface FePc and the Fe metal center of the FePc directly below the
surface layer. The effective mass of the Fe metal chemisorption site on the monolayer
FePc/Au(111) can be calculated similarly whereby the layer directly below the surface
Fe consists of a heavy Au substrate atom. This results in an effective mass of 101 amu
for the Fe metal chemisorption site on the multilayer FePc/Au(111) film and 253 amu
for the Fe metal chemisorption site on the monolayer FePc/Au(111). Therefore, the
inferior mass matching between the NO molecule and the monolayer FePc/Au(111)
film reduces the “heavier” film’s ability to trap NO compared to the “lighter” ordered
multilayer FePc/Au(111) film. In addition to playing a mechanical role in affecting
NO adsorption onto the monolayer FePc film, the Au substrate may affect NO
adsorption by perturbing the FePc electronic structure in the monolayer film compared
to the multilayer FePc film. Although a previous computational study showed that the
NO binding strength onto a single FePc molecule (monomer) and a vertical stack of
three FePc molecules (trimer) are nearly identical, substrate effects on the monolayer
FePc film were not included in the simulations.64 A recent STM study investigated the
electronic structure of a monolayer CoPc/Au(111) film and a trilayer CoPc/Au(111)
film.84 By analyzing the range in bias voltages (-2 V to +2 V) in which the CoPc
molecules were observed, Takada et al showed that the electronic structure of the
monolayer film was more delocalized than the trilayer film suggesting the Au
substrate does perturb the phthalocyanine electronic structure.

In sum, the greater $S_0$ at all $T_s$ and $E_i$ suggests the ordered multilayer FePc film
possesses a greater ability to trap NO onto the aromatics than both the quasi-
amorphous ttbu-FePc and monolayer FePc films. While $S_0$ for the ttbu-FePc and monolayer FePc films are nearly identical, the explanation for the attenuated sticking are not. The lower $S_0$ on the thick ttbu-FePc film is attributed to the exposure of fewer metal, aromatic, and nitrogen sites to the NO beam due to its lower packing density. However, this is not the case for the monolayer FePc film since the packing density of the ordered multilayer FePc and monolayer FePc films are identical. Instead, the lower $S_0$ on the monolayer FePc film is attributed to a reduction in the degree of inelastic collisions due to the heavy Au substrate atoms. In addition, the Au substrate may also play a role in perturbing the electronic structure of the monolayer FePc film to affect NO trapping.

B. NO saturation coverage on multilayer FePc, multilayer ttbu-FePc and monolayer FePc films

Since the area of the FePc molecule occupied by the Fe metal center is small, NO saturation coverage should also be small. A previous study showed that the area occupied by the Fe metal center in the monolayer FePc films was roughly 3%. The normalized NO saturation coverage can be derived from the experimental sticking profiles by integrating the area of the sharp, downward spike and calculating the ratio of this integrated area with respect to the integrated area of the NO sticking profile onto Al(111) for the particular beam energy; this technique is explained in detail in reference 22. It was shown previously that NO has a 1 ML saturation coverage on Al(111). The normalized NO saturation coverage on the ordered multilayer FePc
film versus $T_s$ is shown in Fig 6(a) for all three $E_i$. NO saturation on the ordered multilayer FePc film for all three $E_i$ is approximately 3% from 100 K – 225 K. At temperatures above 225 K, the total saturation coverage gradually decreases. A saturation coverage of 3% is consistent with the NO chemisorption site on the multilayer FePc film being restricted to the Fe metal center whereby the organic component of the molecule acts as precursor physisorption sites prior to NO diffusion to the metal. The attenuation in saturation coverage at higher $T_s$ may be due to NO approaching the desorption temperature from the ordered multilayer FePc film. However, the calculation method used to determine the saturation coverage may also contribute to the decrease in saturation coverage beginning at 225 K. As $T_s$ increases, $S_0$ decreases making the calculation of the area in the spike less accurate since short wide spikes at higher $T_s$ are not as well-defined as the tall narrow spikes at lower $T_s$.

For NO saturation on the quasi-amorphous multilayer ttbu-FePc film, a smaller saturation coverage is expected since the ttbu-FePc film contains a lower surface molecular density than the ordered multilayer FePc film. As discussed above in the Materials and Methods section B, the multilayer ttbu-FePc film is approximately 24% to 42% less dense than the multilayer FePc film. This suggests the total area occupied by the metal centers in the ttbu-FePc film should also be 24% to 42% less than in the ordered multilayer FePc film. Therefore, the area occupied by the Fe metal centers in the quasi-amorphous film should be 2.27% – 1.73%. In contrast, NO saturation on the monolayer FePc and multilayer FePc films should be identical since both films are highly ordered and contain the same areal density. As seen in Fig. 5(b),
NO saturation coverage on the quasi-amorphous ttbu-FePc film is ~2% from 100 K to 175 K; this is less than the 3% observed for the ordered multilayer FePc film and essentially the midpoint of the predicted range for the less dense ttbu-FePc film. As expected, the NO saturation coverage on the monolayer FePc film from 100 K to 175 K is 3% and identical to the saturation coverage on the multilayer FePc film.

While NO saturation coverage on the ordered multilayer FePc film gradually decreases beginning at 225 K, the coverage decrease in the multilayer ttbu-FePc and monolayer FePc films begin at a lower temperature, 175 K. There are two possible explanations. First, NO desorption from the multilayer ttbu-FePc film occurring at a lower temperature than the ordered multilayer FePc film would be consistent with the NO chemisorption well on the Fe metal center being more shallow on the multilayer ttbu-FePc film than on the multilayer FePc film. This hypothesis is consistent with a recent STM study showing the electronic structure of surface CoPc molecules are different on monolayer and trilayer CoPc films on Au(111). However, Tran et al showed that NO binding onto the Fe metal center of a single FePc molecule (monomer), a system with zero possibility for metal-metal interaction and an FePc triple stack (trimer), a system that maximizes the potential for metal-metal interaction, have nearly equivalent exothermicity. The second explanation of lower temperature for attenuation in saturation coverage on the quasi-amorphous ttbu-FePc and monolayer FePc films versus the ordered multilayer FePc film is the error inherent in the calculation method. Increasing T decreases S0 thereby making the calculation of the area in the spike less accurate since the smaller spike at higher temperatures
contains a smaller signal-to-noise ratio than the larger spike at lower sample temperatures. While the slope of the decrease in $S_0$ with $T_s$ are similar for all three phthalocyanine films at all three $E_i$, the magnitude of the decrease in $S_0$ with $T_s$ is greater on the quasi-amorphous multilayer ttbu-FePc and ordered monolayer FePc films than on the ordered multilayer FePc film. It is possible that this discrepancy may create a bias in the calculation of the saturation coverage.

C. Precursor-mediated chemisorption model

For all NO beam energies studied, the $S_0$ observed at 100 K on the various FePc/Au(111) films are large ($0.24 < S_0 < 0.43$) even though the area occupied by the Fe metal center in the ordered multilayer FePc and multilayer ttbu-FePc films are considerably smaller at 3% and 2%, respectively. This suggests NO physisorbs to the aromatics and nitrogens on the FePc molecule prior to chemisorbing onto the Fe metal center. The strong linear dependence of $S_0$ on $T_s$ for all three films and all $E_i$ suggests that increasing the $T_s$ decreases the number of available NO physisorption sites since the shallower physisorption sites are unable to promote NO chemisorption at higher surface temperatures. To quantify the distribution of physisorption sites on the various FePc films, the $S_0$ data for all three films was plotted in an Arrhenius form as discussed in detail in the previous study.\textsuperscript{11} Analyzing the slope of the Arrhenius plot of $S_0$ and inverse $T_s$ provides information on the difference between activation barriers for desorption versus chemisorption from the physisorption sites.
As shown in Fig. 7, the Arrhenius plot for the 0.4 eV NO/ttbu-FePc/Au(111) sticking data requires multiple linear fits to appropriately describe the curve. Note that the Arrhenius fits for NO/monolayer FePc/Au(111) were not shown since the monolayer results were nearly identical to the NO/ttbu-FePc/Au(111) results which have been previous reported.\textsuperscript{11} Fitting the Arrhenius plot to three separate lines (all regression coefficients, $R^2$, were greater than 0.9) results in three barriers to chemisorption for NO adsorption onto the multilayer ttbu-FePc and monolayer FePc films ranging from very small barriers of 10 – 13 meV (100 K to 175 K) and 48 – 70 meV (200 K to 250 K) to slightly larger barriers of 253 – 333 meV (275 K to 300 K). The various barriers to NO chemisorption from 100 K to 300 K suggest that NO physisorption onto the multilayer ttbu-FePc/Au(111) and monolayer FePc/Au(111) films contains many distinct sites and pathways prior to chemisorption.

For the NO/multilayer FePc/Au(111) sticking data, a bi-linear fit sufficiently describes the Arrhenius plot. While the magnitude of barriers to NO chemisorption on the ordered multilayer FePc film are small (7 – 9 meV from 100 K to 175 K and 47 – 51 meV from 200 K to 300 K) and similar to that observed on the multilayer ttbu-FePc and monolayer FePc films, a deviation is observed at higher sample temperatures. In the ordered multilayer FePc film, the barrier to NO chemisorption from 200 K to 250 K extends to 300 K and is consistent with the physisorption paths in the multilayer film being nearly degenerate from 200 K to 300 K. The multiple barriers to chemisorption suggest NO physisorption onto the multilayer FePc film also takes
place at distinct sites and pathways as in the multilayer ttbu-FePc and monolayer FePc films.

2.5 CONCLUSIONS

The King and Wells reflection technique was used to elucidate the chemisorption dynamics of NO on various FePc films. The results show that NO undergoes precursor-mediated chemisorption on all films studied: the ordered multilayer FePc film, the quasi-amorphous multilayer ttbu-FePc film and the ordered monolayer FePc film. The NO sticking probability is greatest on the multilayer FePc film and nearly identical between the multilayer ttbu-FePc and monolayer FePc films. The lower $S_0$ on the monolayer FePc film is ascribed to a lower density of soft phonon modes that may diminish the extent of inelastic collisions to decrease the NO trapping probability of the monolayer film compared to the multilayer films. The $S_0$ on the multilayer ttbu-FePc film may be attributed to fewer metal, aromatic, and nitrogen sites being exposed to the incoming beam due to its lower packing density. The saturation coverage is also less on the multilayer ttbu-FePc film than the ordered monolayer and multilayer FePc films, consistent with the area occupied by the Fe metal being less in the lower areal density ttbu-FePc film than in the monolayer and multilayer FePc films.
2.6 FIGURES

Figure 2.1 Schematic of an (a) iron phthalocyanine molecule and (b) tetra-t-butyl iron phthalocyanine molecule.  ● Fe.  ○ N.  □ C.  ◇ H.
Figure 2.2 Filled-state STM image of (a) ttbu-NiPc on a Au(111) substrate and (b) ordered monolayer CuPc on Au(111). The ttbu-FePc film has a flat surface with short range order. Both images were obtained with -1.0 V sample bias and 0.5 nA tunneling current.
Figure 2.3 Sample NO on multilayer FePc sticking profile illustrating the King and Wells reflection process. The ratio of the partial pressure drop when the inert Pyrex flag is removed at $t_1$ over the partial pressure rise when the gate valve is opened at $t_0$ equals the initial sticking probability at zero coverage.
Figure 2.4 Plot of NO sticking probabilities as a function of sample temperature at (a) varying NO beam energies (0.09 eV = filled circles, 0.26 eV = dashed line, and 0.40 eV = open triangles) for the multilayer FePc film and (b) 0.4 eV NO beam for the multilayer FePc (open squares), multilayer ttbu-FePc (filled triangles) and monolayer FePc (dashed line) films. All error bars shown are for the standard error of eight measurements at each temperature.
Figure 2.5 Plot of NO sticking probability as a function of beam energy at 100 K, 200 K and 300 K for the (a) ordered multilayer FePc and (b) ordered monolayer FePc film. All linear fits have a regression coefficient, $R^2$ greater than 0.95.
Figure 2.6 Plot of NO saturation coverage as a function of sample temperature at (a) varying NO beam energies for a multilayer FePc film and (b) at 0.4 eV NO beam for the multilayer FePc (open squares), multilayer ttbu-FePc (filled triangles) and monolayer FePc (dashed line) films. All error bars shown are for the standard error of eight measurements at each temperature.
Figure 2.7 Arrhenius plots for the 0.4 eV NO beam for the multilayer FePc (open squares) and multilayer ttbu-FePc (filled triangles). The monolayer FePc data was not shown as the results were nearly identical to the ttbu-FePc results.
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CHAPTER THREE

CORRELATION BETWEEN ANALYTE BASICITY, ZNPC BINDING STRENGTH AND SENSOR RESPONSE: AN *AB-INITIO* STUDY

3.1 ABSTRACT

Density functional theory (DFT) simulations including Hartree-Fock exchange were used to determine the binding strength of 12 electron donating analytes to the Zinc metal center of a single molecule Zinc Phthalocyanine (ZnPc monomer). The analyte binding strengths were compared to the analytes’ enthalpy of formation with Boron trifluoride (BF₃) which is a direct measure of their electron donating ability or Lewis basicity. With the exception of the most basic analyte investigated, the ZnPc binding energies were found to be a linear function of analyte basicities. Based on natural population analysis calculations (NPA), analyte complexation to the Zn metal of the ZnPc monomer resulted in limited charge transfer from the analyte to the ZnPc molecule and increased with analyte-ZnPc binding energy. The analyte sensitivities from chemiresistor ZnPc sensor data were proportional to an exponential of the...
binding energies from DFT calculations consistent with sensitivity being proportional to analyte coverage. The good correlation observed suggests DFT is a reliable method for the prediction of chemiresistor MPc binding strengths and sensor response sensitivities.
3.2 INTRODUCTION

Metallophthalocyanines (MPcs) are a group of porphyrin analogs that can form highly ordered, chemically inert, and thermally stable films. They have been extensively studied with both experimental and theoretical techniques. More than 70 phthalocyanines with varying electronic and absorption properties have been synthesized since their chemical properties can be easily manipulated by changing the metal center or substituting functional groups to the organic rings. Their stability and widely varying chemical properties make them an attractive candidate for use in chemical sensors. Jones and Bott showed that two-terminal resistive sensors with different $p$-type MPc films (metal-free H$_2$Pc, PbPc, CoPc, CuPc, NiPc, MgPc and ZnPc) are sensitive to NO$_2$ and Cl$_2$ at low parts per million concentrations. A more comprehensive study by Bohrer et al. revealed that arrays of two-terminal MPc sensors could be used to selectively distinguish between 12 analytes with varying chemical properties. In addition, Yang et al. directly compared the effect of strong and weak binding gas analytes to $p$-type and $n$-type phthalocyanine-based three-terminal field effect transistor sensors.

Although the experimental and theoretical literature pertaining to MPc sensor applications is extensive, only a few experimental studies have examined the gas chemisorption of a large array of analytes onto MPcs. Instead, most experimental studies focus on the sensor responses of one or two gas analytes onto
multiple MPcs. Existing theoretical investigations of MPcs have focused primarily on the electronic structure of an isolated, single molecule MPc (monomer), the film in its β-crystalline form, or on the molecular interaction of the monomer with a substrate. A few computational studies have investigated the interaction of an analyte with the MPc, but most of these studies are motivated either by analyte binding to the hydrogen bridge of the metal-free phthalocyanine or the binding of a single analyte onto the metal center of the MPc. While another computational study reported the binding of an electron donating and electron accepting analyte to FePc at seven different plausible binding sites on the FePc molecule, only two analytes were studied. To our knowledge, there have been no published theoretical studies examining the binding strength of a variety of gas analytes to an MPc monomer.

This study attempts to investigate the adsorption strength of 12 analytes spanning a wide range of Lewis basicities based on the $-\Delta H_{BF3}$ scale to the Zn metal of the ZnPc monomer using DFT. The $-\Delta H_{BF3}$ scale is an indicator of the ability of an analyte to donate electrons and is an enthalpy scale based on adduct formation with BF$_3$. The simulated binding strengths to ZnPc are compared to their enthalpy of formation with BF$_3$. The DFT calculated binding strengths are also compared to current response data from a recent sensor study using chemiresistive ZnPc sensors by Bohrer et al. Finally, charge transfer upon analyte binding was also investigated using NPA calculations.
3.3 COMPUTATIONAL TECHNIQUES

Optimizations of all systems—the ZnPc monomer, all analytes and the ZnPc-analyte complexes—were performed using Gaussian03, revision D.01 with the Becke 3-parameter hybrid exchange functional and Lee-Yang-Parr gradient corrected electron correlation functional (B3LYP) with the 6-31G* basis. All initial structures were built using Gaussview, version 2.08. A schematic of the ZnPc monomer and the analytes studied can be found in Figs. 1(a, b), respectively. The bond lengths and bond angles of the calculated ground state structures for ZnPc (D4h), dichloromethane (Dichlo), nitromethane (Nitro), acetonitrile (Aceto), cis-2-butanone (2-But), water, di-n-butylether (n-But), trimethylphosphate (TMP), dimethylmethylphosphonate (DMMP), isophorone (Iso), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and triethylamine (TEA) agrees with those determined by other computational and experimental studies to within 0.03Å and 0.02º.

Only binding to the Zn metal center of the ZnPc monomer was investigated since numerous experimental and theoretical studies have shown that preferential binding to the metal center occurs and experimental data shows the sensor response differs for a given analyte on different MPc films consistent with bonding to the metal centers. Various initial geometries of analyte binding to the Zn metal center were sampled to determine the lowest energy binding conformation for each
analyze. For example, eight conformational isomers were investigated for the binding of DMF to the ZnPc metal center via the oxygen atom of the DMF molecule; Fig. 2 shows the initial geometry of two of the more than eight conformations investigated for the ZnPc-DMF complex. Fig. 2(a) shows DMF binding through the double-bonded oxygen atom of DMF to the Zn metal of the ZnPc monomer. In this figure, the backbone of the DMF molecule eclipses the Zn-N bond of the ZnPc molecule to give a torsional angle, $\phi = 0^\circ$, while the Zn-O-C angle is linear with $\theta = 180^\circ$. Three other ZnPc-DMF conformations sampled includes varying $\theta$ at 15$^\circ$ increments ($\theta = 165^\circ$, 150$^\circ$ and 135$^\circ$). The remaining four complexes sampled involve rotating the DMF molecule by 45$^\circ$ about $\phi$ in conjunction with varying $\theta$ at 15$^\circ$ increments from 180$^\circ$ to 135$^\circ$. Fig. 2(b) shows a side view of DMF binding to the Zn metal where $\phi = 45^\circ$ and $\theta = 150^\circ$. Additionally, binding through the nitrogen atom of the DMF molecule to the Zn metal of the ZnPc monomer was also investigated; this was approximately 58 kJ/mol less exothermic than binding at the double-bonded oxygen atom; therefore, sampling DMF binding to the Zn metal via the nitrogen atom was subsequently abandoned.

While binding through both the nitrogen and oxygen atoms were sampled for DMF binding to ZnPc, only binding via the nitrogen atom was investigated for acetonitrile (Aceto) and TEA. For cis-2-butanone (2-But), water, $n$-butylether ($n$-But) and isophorone (Iso) only binding through the oxygen atom was sampled. For TMP and DMMP, binding through the oxygen double-bonded to the phosphorous was
investigated. For DMSO, binding through both the oxygen and electron rich sulfur were sampled; DMSO binding through the double-bonded oxygen was found to be 55 kJ/mol more exothermic than binding through the sulfur atom. In all cases, geometry optimizations of numerous ZnPc-analyte complexes were investigated to determine the lowest binding energy conformational isomer for each analyte. The final, optimized structures for all analyte-ZnPc complexes can be found in Figs. 3(A–L).

For TEA, additional molecular dynamics (MD) simulations using the Vienna ab-initio simulations package (VASP)$^{33-35}$ were used in an attempt to locate the global minimum ZnPc-TEA binding conformation since the ZnPc-TEA complex contains a large number of degrees freedom (231) compared to all other ZnPc-analyte complexes. Prior to beginning the MD simulations, geometry optimizations of two of the most exothermic configurations of the ZnPc-TEA complex as determined from Gaussian03 were performed using VASP with the PW91 variety of the generalized-gradient approximation (GGA), using ultrasoft Vanderbilt pseudopotentials as supplied within VASP,$^{35-37}$ and a single k-point (located at the gamma point). The kinetic energy cutoff was set to 400 eV. All three systems were geometrically relaxed to a convergence tolerance of 0.01 eV/Å. The two VASP-optimized ZnPc-TEA complexes were heated to 425 K for 1 ps followed by cooling to 0 K over a 1 ps period. Once the MD simulations were complete, the structures from the last timestep were reoptimized in G03 for a consistent and proper comparison of binding energies with respect to all the other analytes studied.
All systems were verified to be minima by evaluating the Hessian matrix in G03. Only complexes containing no imaginary frequencies are discussed in this study. The binding energies ($\Delta E_{\text{bind}}$) were calculated as:

$$\Delta E_{\text{bind}} = E(\text{ZnPc + Analyte}) - E(\text{ZnPc}) - E(\text{Analyte})$$

(1)

where $E(\text{ZnPc + Analyte})$, $E(\text{ZnPc})$ and $E(\text{Analyte})$ represent the total energies of the ZnPc-analyte complex, the gas-phase ZnPc, and the gas-phase analyte, respectively. All binding energies discussed include the correction for the zero-point vibrational energy (ZPE). The ZPE correction ($\Delta E_{\text{ZPE}}$) is calculated as:

$$\Delta E_{\text{ZPE}} = E_{\text{ZPE}}(\text{ZnPc + Analyte}) - E_{\text{ZPE}}(\text{ZnPc}) - E_{\text{ZPE}}(\text{Analyte})$$

(2)

where $E_{\text{ZPE}}(\text{ZnPc + Analyte})$, $E_{\text{ZPE}}(\text{ZnPc})$ and $E_{\text{ZPE}}(\text{Analyte})$ represent the ZPE correction for the ZnPc-analyte complex, the gas-phase ZnPc, and the gas-phase analyte, respectively. Counterpoise corrections using the Boys and Bernardi counterpoise correction scheme as supplied within Gaussian 03 were also included to account for basis set superposition errors (BSSE).\textsuperscript{109,110} The BSSE correction ($\Delta E_{\text{BSSE}}$) is calculated as:

$$\Delta E_{\text{BSSE}} = E_{\text{BSSE}}(\text{ZnPc + Analyte}) - E_{\text{BSSE}}(\text{ZnPc}) - E_{\text{BSSE}}(\text{Analyte})$$

(3)
where $E_{BSSE}(\text{ZnPc + Analyte})$, $E_{BSSE}(\text{ZnPc})$ and $E_{BSSE}(\text{Analyte})$ represent the BSSE correction energy for the ZnPc-analyte complex, the gas-phase ZnPc fragment, and the gas-phase analyte fragment, respectively. Therefore, the ZPE and BSSE corrected binding energies ($\Delta E_{corr}^{bind}$) are simply calculated as:

$$\Delta E_{corr}^{bind} = \Delta E_{bind} + \Delta E_{ZPE} + \Delta E_{BSSE}$$

(4)

Only $\Delta E_{corr}^{bind}$ energies will be discussed in this paper.

### 3.4 RESULTS AND DISCUSSION

#### A. ZnPc binding versus Lewis basicity

Table I lists the twelve analytes studied along with their Lewis basicities based on the $-\Delta H_{BF3}$ scale where dichloromethane is the weakest base with $-\Delta H_{BF3} = 10 \pm 0.03$ kJ/mol and TEA is the strongest ($-\Delta H_{BF3} = 135.87 \pm 1.67$ kJ/mol). Note that the $-\Delta H_{BF3}$ enthalpy value listed for isophorone has been corrected by 11.8 kJ/mol since its enthalpy value has been overestimated due to the ability of BF$_3$ to bind the alkene as well as the oxygen atom. Additionally, Lewis basicity values for DMMP and water are not available in the literature and hence were extrapolated from an exponential fit of sensor sensitivity data to $-\Delta H_{BF3}$ values.
The results of the DFT calculated adsorption energies for all 12 analytes binding to the Zn metal of the ZnPc monomer are plotted against Lewis basicity in Fig. 4. The least basic analyte (Dichlo) is the weakest binder to ZnPc with an exothermicity of -0.81 kJ/mol. The binding strength of the analytes to ZnPc increases as its basicity increases. For example, the basicities of 2-butanone (-76.07 kJ/mol) and DMF (-110.49 kJ/mol) are roughly two and three times greater than that of nitromethane (-37.63 kJ/mol) and their ZnPc binding strengths are also two and three times greater than nitromethane (-21.87 kJ/mol and -35.87 kJ/mol, respectively versus -13.81 kJ/mol). Fitting the experimentally determined enthalpies of formation to BF$_3$ versus binding strengths to ZnPc for all 12 analytes results in a linear dependence with a regression coefficient, $R^2 = 0.73$. Clearly, the outlier in the linear fit is TEA, with a relatively weak binding strength to ZnPc (-30.49 kJ/mol) despite being the most basic analyte in the study (-135.87 kJ/mol). Omitting TEA from the fit results in a linear dependence between the analyte Lewis basicities and their coordination strengths to ZnPc with an improved $R^2 = 0.88$ and slope = 2.44.

Almost half the analytes studied, have a DFT binding strength to the Zn metal which is greater than the TEA DFT binding strength. The DFT calculations show that DMSO, with a basicity of $-105.34 \pm 0.36$ kJ/mol, binds the strongest to ZnPc with an exothermicity of $-38.59$ kJ/mol. Initially, the contrast between the weak binding strength of TEA with respect to its strong Lewis basicity was attributed to obtaining a local minimum structure for the ZnPc-TEA complex instead of the global minimum
structure. This was the initial hypothesis primarily due to the presence of the large number of degrees of freedom in the ZnPc-TEA complex; a large number of rotational configurations could be sampled as a result of rotation about the nitrogen-carbon and carbon-carbon $\sigma$-bonds of the TEA molecule. Geometry optimizations for six different ZnPc-TEA conformational isomers were sampled to give exothermic binding strengths ranging from -4.65 kJ/mol to -21.25 kJ/mol. Due to the large number of conformational isomers that could result from the ZnPc-TEA complex, MD simulations were also incorporated in an attempt to obtain a more energetically favored ZnPc-TEA structure. The ZnPc-TEA structure obtained through performing MD simulations as described in the Computational Methods section resulted in a structure that was 9.24 kJ/mol lower in energy than the most stable ZnPc-TEA configuration obtained only from G03 geometry optimizations. While this MD optimized structure is lower in energy than the structures that did not undergo a heating and cooling cycle, there still remains a large discrepancy in ZnPc binding energies for TEA compared to the other, less basic analytes investigated. This energy difference can be attributed to the demanding steric effects of the ethyl groups on the TEA molecule upon binding to the Zn metal. For binding to BF$_3$, the ethyl groups in TEA do not play as large a role in steric hindrance since the BF$_3$ molecule is small. In contrast, the large ZnPc molecule contains a square planar configuration where the pyrrole nitrogens and organic rings may act to prohibit the bulky ethyl groups from
fully relaxing around the Zn atom. This is consistent with numerous studies which have documented the steric effects of TEA.\textsuperscript{112,113}

With the exception of TEA, ZnPc binding of the remaining analytes results in a reasonable linear correlation to their Lewis basicities. Since the basicity of a molecule is a measure of its ability to donate electrons, complexation of the 12 electron donating analytes to the Zn metal may result in a transfer of electrons from the analyte to the ZnPc monomer. Charge transfer has been repeatedly cited as the mechanism in which MPc-based sensors operate.\textsuperscript{48,114,115} To determine the degree of charge transfer, the atomic charges of the ZnPc monomer and the ZnPc-analyte complexes were calculated using NPA calculations within the B3LYP functional and 6-31G* basis.\textsuperscript{116} Mulliken charges were not used as they are notorious for their basis set dependence.\textsuperscript{117,118} The magnitude of charge transfer (\(\Delta q_{\text{ZnPc}}\)) is then determined by taking the difference of the total charge of the ZnPc molecule in the ZnPc-analyte complex minus the total charge of the ZnPc monomer. The charge transfer is plotted as a function of ZnPc binding strength as shown in Fig. 5. The weakest binder, dichloromethane, results in a transfer of 0.014e\textsuperscript{−} to the ZnPc monomer whereas the strongest binder, DMSO, results in the greatest transfer of electrons to the ZnPc monomer (0.053e\textsuperscript{−}). Regardless of where the analyte lies on the basicity scale, analyte adsorption onto the ZnPc monomer results in a small charge transfer from the analyte to the ZnPc consistent with the electron donating nature of the basic analytes. The small charge transfer for these weakly bound analytes is consistent with that observed in a previous study using
the Bader, atoms in molecules method that showed electron donating physisorbates donated 0.07e\textsuperscript{-} to the FePc metal center.\textsuperscript{51,64,119} Additionally, analysis of the plot shows a weak linear dependence between the magnitude of electron donation from the analyte to the ZnPc monomer and their ZnPc binding energies (R\textsuperscript{2} = 0.67). Although the DFT calculations show charge transfer does occur upon analyte binding to the Zn metal of the ZnPc monomer, this charge transfer is limited. This suggests that analyte sensitivities will be dominated by analyte binding energies to the MPc instead of charge transfer since analyte coverage is an exponential function of analyte binding energy whereas the DFT simulations show that charge transfer is only a linear function of the analyte binding energy.

In sum, the magnitude of ZnPc binding strengths and limited charge transfer observed for these analytes suggest that the more basic analytes only weakly chemisorb whereas the less basic analytes physisorb to the Zn metal center. In the case of dichloromethane, adsorption onto the Zn metal consists of weak physisorption. The small charge transfer is still consistent with ZnPc films being very sensitive to the presence of analytes because the films have low intrinsic carrier concentration and very weak surface doping by O\textsubscript{2} which transfers even less than all the analytes in this study.\textsuperscript{120-122}

**B. ZnPc binding versus ZnPc chemiresistor sensor data**

To investigate how analyte binding energies relate to experimental sensor data, the DFT calculated binding energies were compared to ZnPc sensor data. Details on
chemiresistor sensor fabrication and device measurements can be found in Reference 13. Briefly, the sensors are two-terminal interdigitated electrode (IDEs) devices consisting of Si (100) substrates with a 1 μm thick wet oxide. There are 45 electron beam evaporated gold finger pairs, each of which are spaced 5 μm apart with an electrode width and thickness of 2 mm and 45 nm, respectively. 50nm thick ZnPc films were then deposited by organic molecular beam epitaxy. The sensor measurements were performed in a stainless steel chamber with SiO2 passivated walls and an internal volume of 15 cm³. The sensor devices were operated at 8 V to ensure all measurements are done in the space-charge limited conductivity (SCLC) regime. Measurements performed within the SCLC regime is essential as it eliminates MPc/electrode interface effects on chemical sensing. The sensors were exposed to analyte vapors at a 500 cm³/min flow rate of varying concentrations ranging from 90 ppm to 900 ppm. It has been shown that a linear dependence between sensor response (percent current change \(\Delta I/I_{\text{baseline}} \times 100\) at constant voltage) and analyte concentration exists in the region where the largest change in sensor current occurs upon analyte exposure. This region is considered the “initial fast region” and was systematically determined to occur within the first 5 minutes of dosing with analyte. As a result, all sensors were exposed to analyte vapors for 5 minutes to allow for a quantitative comparison of sensor response to analyte concentration. The relationship between sensor response and analyte concentration in the fast region was used to obtain ZnPc sensitivities (%/ppm) determined from the slope of the linear fits of
response versus concentration. Additionally, it has been suggested that MPc sensor responses occurring within the first 5 minutes correspond to analyte adsorption onto metal centers free of atmospheric dopants such as O₂. Therefore, the gas adsorption model used in this computational study where the analyte adsorbs directly onto the Zn metal center of the ZnPc molecule is an appropriate model system.

Fig. 6 shows a plot of the experimentally determined ZnPc sensitivities versus the DFT calculated ZnPc binding energies for all 12 analytes. Note that positive sensitivities are for current gains while negative sensitivities are for current losses. In contrast to the linear dependence observed between analyte basicity and ZnPc binding strength, an exponential dependence exists for ZnPc sensitivities and binding strengths. An exponential dependence between sensitivity and binding strength is consistent with established models of surface coverage and binding energy. Although an exponential fit of all the data results in a poor regression coefficient R² = 0.18, removal of TEA from the fit due to its steric effects with respect to ZnPc binding in DFT calculations as discussed above, results in very good agreement between ZnPc sensitivities and binding strengths with R² = 0.94. This indicates that ZnPc binding sensitivities are a strong exponential function of ZnPc binding energies. Since sensor sensitivities are an exponential function of binding energies, even small differences in MPc binding strengths between analytes would result in noticeable differences in their sensor sensitivities and responses thereby making MPcs an ideal material for the selective detection of an array of gas analytes. Finally, the good correlation observed
suggests that DFT can be a reliable method for prediction of chemiresistor MPc binding sensitivities and sensor response.

3.5 CONCLUSIONS

DFT simulations were used to determine the binding strength of 12 electron donating analytes to the Zinc metal of a ZnPc monomer. The analyte binding strengths were shown to be linearly dependent upon their Lewis basicity based on the $-\Delta H_{BF3}$ scale. NPA charge transfer calculations show that electron donating analyte complexation to ZnPc results in limited charge transfer from the analyte to the ZnPc monomer. The analyte sensitivities from chemiresistor ZnPc sensor data were proportional to an exponential of the binding energies from DFT calculations consistent with sensitivity being proportional to analyte coverage. The results show MPcs can make for highly selective sensors since MPcs can even select for analytes with similar electronic properties. In sum, the good correlation observed suggests that DFT is a reliable method to predict relative chemiresistor MPc analyte sensitivities.
Figure 3.1 Schematic of an (a) isolated, single molecule zinc phthalocyanine molecule (ZnPc monomer) and (b) all twelve electron donating analytes studied.
Figure 3.2 Schematic of the initial geometry of two of more than eight conformational isomers sampled for DMF binding to ZnPc.  

a) Double-bonded oxygen atom of DMF binding to the Zn metal where the torsional angle, $\phi = 0^\circ$, is formed by the C-N bond lying in the DMF molecular plane eclipses the Zn-N bond of the ZnPc molecule. Other ZnPc-DMF isomers consist of rotating the DMF molecule by $45^\circ$ about this torsional angle, $\phi$; the configuration rotated by $45^\circ$ will be referred to as “staggered.”

b) Side view of DMF binding to the Zn metal where the DMF molecule is staggered with respect to the Zn-N bond. The DMF molecule is bonded such that the Zn-O-C angle, $\theta$, is $150^\circ$. The remaining ZnPc-DMF isomers are formed by varying $\theta$ at $15^\circ$ increments from $180$ to $135^\circ$. 

Figure 3.3A Schematic of the lowest energy, optimized Dichlo-ZnPc complex. a) Chlorine atom of Dichlo binding to the Zn metal. This structure contains a Zn-Cl distance of $R_{Zn-Cl} = 3.16$ Å and a torsional angle, $\theta = 45^\circ$. b) side view of Dichlo binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The Dichlo molecule is bonded such that the Zn-Cl-C angle, $\theta = 101^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\varphi = 167.71^\circ$. 

\[ R_{Zn-Cl} = 3.16 \, \text{Å} \]
Figure 3.3B Schematic of the lowest energy, optimized Nitro-ZnPc complex. a) Oxygen atom of Nitro binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.29$ Å and a torsional angle, $\theta = 45^\circ$. b) side view of Nitro binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The Nitro molecule is bonded such that the Zn-O-N angle, $\theta = 125^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\varphi = 159.34^\circ$. 
Figure 3.3C Schematic of the lowest energy, optimized Ace-ZnPc complex. a) Nitrogen atom of Ace binding to the Zn metal. This structure contains a Zn-N distance of $R_{Zn-N} = 2.21$ Å. b) Side view of Ace binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The Ace molecule is bonded such that the Zn-N-C angle, $\theta$, is 180º and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\phi$, is 155.97º.
Figure 3.3D Schematic of the lowest energy, optimized 2-But-ZnPc complex. a) Oxygen atom of 2-But binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.18$ Å and a torsional angle, $\theta = 45^\circ$. b) Side view of 2-But binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The 2-But molecule is bonded such that the Zn-O-C angle, $\theta = 139^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\varphi = 155.93^\circ$. 
Figure 3.3E Schematic of the lowest energy, optimized Water-ZnPc complex. a) Oxygen atom of Water binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.21$ Å and a torsional angle, $\theta = 45^\circ$. b) Side view of Water binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The Water molecule is bonded such that the Zn-O-H angle, $\theta = 111^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\varphi = 158.31^\circ$. 
Figure 3.3F Schematic of the lowest energy, optimized $n$-But-ZnPc complex. a) Oxygen atom of $n$-But binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.18$ Å and a torsional angle, $\theta = 45^\circ$. b) Side view of $n$-But binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The $n$-But molecule is bonded such that the Zn-O-C angle, $\theta = 122^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\phi = 155.71^\circ$. 
Figure 3.3G Schematic of the lowest energy, optimized Iso-ZnPc complex. a) Oxygen atom of Iso binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.14 \text{ Å}$ and a torsional angle, $\theta = 45^\circ$. b) Side view of Iso binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The Iso molecule is bonded such that the Zn-O-C angle, $\theta = 138^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\phi = 154.54^\circ$. 
Figure 3.3H Schematic of the lowest energy, optimized TMP-ZnPc complex. a) Oxygen atom of TMP binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.11$ Å. b) side view of TMP binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The TMP molecule is bonded such that the Zn-O-P angle, $\theta = 163^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that N-Zn-N angle, $\phi = 154.43^\circ$. 
Figure 3.3I Schematic of the lowest energy, optimized DMMP-ZnPc complex. a) Oxygen atom of DMMP binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.11$ Å. b) Side view of TMP binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The DMMP molecule is bonded such that the Zn-O-P angle, $\theta = 146^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that N-Zn-N angle, $\phi = 154.06^\circ$. 
Figure 3.3J Schematic of the lowest energy, optimized DMSO-ZnPc complex. a) Oxygen atom of DMSO binding to the Zn metal. This structure contains a Zn-O distance of $R_{\text{Zn-O}} = 2.11$ Å. b) Side view of DMSO binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The DMSO molecule is bonded such that the Zn-O-S angle, $\theta = 140^\circ$ and the Zn atom protrudes out of the ZnPc molecular plane such that N-Zn-N angle, $\varphi = 153.37^\circ$. 
Figure 3.3K Schematic of the lowest energy, optimized DMF-ZnPc complex. a) Oxygen atom of DMF binding to the Zn metal. This structure contains a Zn-O distance of $R_{Zn-O} = 2.13$ Å and a torsional angle, $\theta = 45^\circ$. b) side view of DMF binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The DMF molecule is bonded such that the Zn-O-C angle, $\theta = 122^\circ$ and the N-Zn-N angle, $\varphi = 154.93^\circ$. 
Figure 3.3L Schematic of the lowest energy, optimized TEA-ZnPc complex. a) Nitrogen atom of TEA binding to the Zn metal. This structure contains a Zn-N distance of $R_{Zn-N} = 2.31$ Å. b) Side view of TEA binding to the Zn metal emphasizing protrusion of Zn metal from the ZnPc molecular plane. The TEA molecule is bonded such that the Zn-N-C angle, $\theta$, is 103° and the Zn atom protrudes out of the ZnPc molecular plane such that the N-Zn-N angle, $\phi$, is 149.80°.
Figure 3.4 Linear fit of Lewis basicities based on the $-\Delta H_{BF3}$ enthalpy scale versus the DFT calculated adsorption energies $-\Delta E_{corr}^{bind}$. The linear fit shown omits TEA to give a slope of 2.44 and regression coefficient, $R^2 = 0.88$. Including TEA in the fit lowers $R^2$ slightly to 0.73. The error bars shown have been compiled by Reference 21.
Figure 3.5 Linear fit of the NPA calculated charge transfer after analyte adsorption $\Delta q_{ZnPc}$ values versus $-\Delta E_{corr\text{ bind}}$ to give a reasonable fit with $R^2 = 0.67$. Note that the small degree of charge transfer observed may be at the lower limits of the method.
Figure 3.6 Curve of ZnPc sensitivities \([\Delta I/I_{baseline} \times 100]/\text{analyte concentration}\)] versus \(-\Delta E_{corr}^{bind}\) for all 12 analytes. The exponential fit shown omits TEA to give a good fit with \(R^2 = 0.94\). Including TEA results in a poor exponential fit with \(R^2 = 0.18\), clearly showing TEA is an outlier. The error bars shown are a standard deviation of 6 slopes from the linear fit of ZnPc sensor response versus analyte concentration from Reference 12.
# 3.7 TABLES

Table 3.1 Table of analytes and their $-\Delta H_{BF3}$ enthalpy values. All values listed are from Reference 21 except for water$^a$ and DMMP$^b$ which were extrapolated from ZnPc sensor data in Reference 12. The basicity value listed for isophorone$^c$ has been corrected for binding through the alkene (Refs 13 and 52). Abbreviations: Dichlo = dichloromethane, Nitro = nitromethane, Aceto = acetonitrile, 2-But = 2-butanone, n-But = di-$n$-butylether, Iso = isophorone, TMP = trimethylphosphate, DMMP = dimethylmethylphosphonate, DMSO = dimethylsulfoxide, DMF = N,N-dimethylformamide, TEA = triethylamine.

<table>
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<tr>
<th>Analytes</th>
<th>$-\Delta H_{BF3}$ (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlo</td>
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<tr>
<td>Nitro</td>
<td>37.63 ± 0.56</td>
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<tr>
<td>Aceto</td>
<td>60.39 ± 0.46</td>
</tr>
<tr>
<td>2-But</td>
<td>76.07 ± 0.33</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>Iso$^c$</td>
<td>78.76 ± 0.41</td>
</tr>
<tr>
<td>TMP</td>
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</tr>
<tr>
<td>DMMP$^b$</td>
<td>104.0 ± 12.9</td>
</tr>
<tr>
<td>DMSO</td>
<td>105.34 ± 0.36</td>
</tr>
<tr>
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</tr>
<tr>
<td>TEA</td>
<td>135.87 ± 1.67</td>
</tr>
</tbody>
</table>
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References


30 B. Szczepaniak and P. Bragiel, Vacuum 46 (5-6), 465 (1995).


42 P. Redhead, Vacuum 12, 203 (1962).


74 I. Chizhov, G. Scoles, and A. Kahn, LANGMUIR 16 (9), 4358 (2000).


